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POLYNITROGEN CHEMISTRY

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UNIVERSITY OF SOUTHERN CALIFORNIA

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Final Report

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Polynitrogen Chemistry

Final Report under Contract FA9550-10-1-0357

Covering the time period 1 July, 2010 – 30 June, 2013

Prepared for

The Air Force Office of Scientific Research, Arlington, VA

by

Karl O. Christe, Ralf Haiges and Martin Rahm

24 September, 2013

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Foreword

This report describes a three year effort carried out between 1 July, 2010 and 30 June, 2013 at the University of Southern California, Los Angeles, for the Air Force Office of Scientific Research with Drs. Ken Caster and Michael Berman serving as the Program Managers. Prof. Karl Christe was the PI and was supported by Prof. Ralf Haiges, Dr. Martin Rahm, Dr. Igor Fedorov, Guillaume Belanger-Chabot, and Drs. William Wilson, and Ross Wagner.

Summary

A highly productive 3-year research program was carried out in the area of high-energy polynitrogen and high-nitrogen chemistry, resulting in the discovery and characterization of numerous novel polynitrogen and polyazide compounds. The work benefitted greatly from the synergy between theoretical calculations and chemical synthesis, and resulted in 15 journal publications, the presentation of 29 invited papers at international and national conferences, and four awards.

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Objectives

The specific goals of this program were basic research in the advancement of energetic materials chemistry by theoretical predictions, the synthesis and characterization of energetic materials with particular emphasis on polynitrogen and high-nitrogen chemistry, and the development of better understanding of the structures and bonding relationships in energetic materials. To achieve these goals, we have heavily relied on the exploitation of the synergy between theory and synthesis. Other goals were the training of a new generation of energetic material scientists and the dissemination of our results through publications in high impact factor journals and the presentation of key lectures at major international and national conferences.

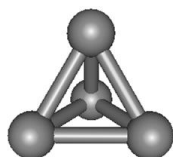
Introduction

The great potential of polynitrogen chemistry for energetic materials was discovered by theoretical predictions under the AFOSR HEDM program which was initiated in 1986. However, no systematic experimental efforts were carried out to verify this concept until DARPA initiated in 1998 a synthesis program. Of the numerous DARPA funded studies, only the one led by Karl Christe which succeeded in synthesizing the stable and insensitive N_5^+ cation in 1999.¹⁻⁴ The same group also demonstrated in 2002 the existence of the *cyclo*- N_5^- anion by electron spray ion mass spectroscopy.⁵ This anion is isoelectronic with the *cyclo*-pentadienide anion and one could envision a wealth of inorganic ferrocene-type chemistry using *cyclo*- N_5^- . Although several dozen theoretical publications have predicted the stability of such ferrocene analogues, the bulk synthesis of an N_5^- salt has not been realized so far.^{6,7} Similarly, the synthesis of polymeric nitrogen or any other form of a room-temperature stable nitrogen allotrope has not been achieved to date.

During previous work by our group, it had become increasingly clear that the synthesis of an ionic polynitrogen compound, consisting of a polynitrogen cation and a polynitrogen anion, is not feasible.⁸ This is due to the fact that the first ionization potential of a neutral species is always much higher than its electron affinity. The difference between the two would have to be made up for by the lattice energy of the ionic solid. Since these lattice energies, even for a solid

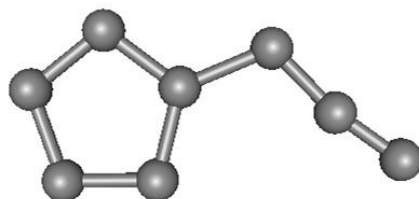
with relatively small ions, should not exceed ~ 160 kcal/mol,⁹ they are insufficient to compensate for the large differences between the first ionization potentials and the electron affinities (for example, for N_2 and N_3 , these differences are 305 and 222 kcal/mol, respectively). This is in accord with the general observation that no ionic allotropes are known for any element, and from the previous failure to prepare $N_5^+N_3^-$.⁸ Therefore, a successful preparation of a nitrogen allotrope needed to be directed toward the synthesis of covalent neutral polynitrogen molecules.

One excellent target compound for a covalent neutral polynitrogen was tetrahedral N_4 .¹⁰



This molecule has been predicted to possess a barrier to decomposition to two N_2 molecules of 60 kcal/mol. Although Radziszewski and coworkers had observed for microwave discharged N_2 infrared¹¹ and Raman¹² spectra in a N_2 matrix at 6 K which showed frequencies close to those predicted for $N_4(T_d)$,¹³ the observed $^{14}N/^{15}N$ isotopic shifts did not exhibit the correct separations and caused serious doubt whether these authors had indeed observed N_4 . Therefore, alternative synthetic methods were explored to either confirm or disprove the previous claim for N_4 .

Other potential candidates for neutral covalent polynitrogen molecules with high kinetic stability include pentazolylazide (*c*- N_5 - N_3),



dipentazolylidiazine (*cyclo*- N_5 - $N=N$ -*cyclo*- N_5), and bis-pentazole (*cyclo*- N_5 -*cyclo*- N_5).^{10,14}

To the best of our knowledge, this type of research was not being pursued in any other laboratory due to its huge technical challenges. The only recent research on nitrogen allotropes involved diamond anvil cell experiments requiring the use of extreme pressures and temperatures.¹⁵ Therefore, the synthesis of a nitrogen allotrope which would be metastable under normal conditions remained an enormous challenge to synthetic chemistry. Needless to say, such an achievement would dwarf, for example, the synthesis and characterization of another carbon allotrope, such as buckminster fullerene. In addition to purely scientific interest, such an achievement would also be of enormous practical interest for the chemistry of High Energy Density Materials (HEDM), providing more powerful and totally green novel explosives and propellants. Even if only partial success could be achieved along these lines, we could expect interesting novel HEDM compounds emanating from this work as a spin off and providing insight into the limitations of HEDM synthesis.

In addition to the area of polynitrogen chemistry, we were interested in high-nitrogen compounds and, particularly, in polyazides. These materials are extremely energetic due to one azido ligand contributing about 80 kcal/mol of endothermicity to a compound, thus making them of great interest for primary and secondary explosives. Since fluorine compounds are in most cases the required starting materials for our reactions, we have also explored the synthesis and characterization of some fluorine compounds. Furthermore, we are using high level quantum chemical calculations for the prediction of the stability and activation energy barriers of our target molecules and, therefore, have a strong interest in this field.

Results and Discussion

Polynitrogen Chemistry

We have acquired and assembled all the required hardware and the spectrometer for matrix isolation spectroscopy. This will allow us to repeat the Radziszewski experiments^{11,12} in the future. We have also explored the possibility of preparing tetrahedral N₄ by low-temperature (-196 °C) electric glow discharge thus avoiding the drawbacks of a microwave discharge. The discharge was carried out next to a -210 °C cold wall to quench any polynitrogen formed. Nitrogen, as well as mixtures of nitrogen with argon, krypton and xenon were discharged at various pressures and voltages to allow for the generation of the ²N and ³N₂ excited states, predicted necessary for the formation of N₄. The bulk of the unreacted dinitrogen was pumped off at -196 °C and the solid residue was characterized by low-temperature Raman spectroscopy. No evidence for a polynitrogen was found and only nitrogen oxides were observed resulting from the reaction with the glass vessel and an oxide film on the copper electrodes.

The formation of the N₃NOF⁺ and N₇O⁺ cations from the reaction of NOF₂⁺SbF₆⁻ with HN₃ in anhydrous HF solution was established by low-temperature vibrational and NMR spectroscopy. The N₇O⁺ cation decomposes at elevated temperature to N₅⁺ which provides a new and more convenient synthesis of N₅⁺, particularly of ¹⁵N labeled N₅⁺.¹⁶

Since N₂F⁺ is the key precursor for the synthesis of N₅⁺,¹ a comprehensive study of N₂F₂ chemistry was carried out. The first ordered crystal structure of N₂F⁺ was obtained showing that the bond distances in this cation are among the shortest known N-N and N-F bonds (highlighted as cover page in Inorganic Chemistry).¹⁷

Polyazide Chemistry

In the field of polyazide chemistry, remarkable progress was achieved resulting in four major publications in *Angewandte Chemie* and *Inorganic Chemistry*. The first binary vanadium(IV) azides, V(N₃)₄ and [V(N₃)₆]²⁻, and vanadium(V) azide, V(N₃)₆⁻, have been prepared and characterized. At ambient temperature, the neutral tetraazide and V(N₃)₆⁻ are very sensitive and highly explosive but the [V(N₃)₆]²⁻ anion, particularly when combined with a large

inert counter ion, is more manageable. Furthermore, the $\text{V}(\text{N}_3)_6^-$ anion is the first binary vanadium(V) species containing a ligand other than fluorine or oxygen.¹⁸

In main group 13, the extremely shock-sensitive group 13 triazides $\text{Ga}(\text{N}_3)_3$, $\text{In}(\text{N}_3)_3$, and $\text{Tl}(\text{N}_3)_3$ were prepared in SO_2 and CH_3CN solutions. The use of the corresponding fluoride starting materials and SO_2 as a solvent provided a convenient synthesis for the neat free triazides and firmly established the existence of thallium triazide. In CH_3CN solution, the new $\text{M}(\text{N}_3)_3 \cdot \text{CH}_3\text{CN}$ donor-acceptor adducts were obtained. Reactions of the triazides with either stoichiometric amounts or an excess of tetraphenyl-phosphonium azide in CH_3CN solution yielded exclusively the novel $[\text{Ga}(\text{N}_3)_5]^{2-}$, $[\text{In}(\text{N}_3)_6]^{3-}$ and $[\text{Tl}(\text{N}_3)_6]^{3-}$ anions, the first examples of multiply charged group 13 polyazido anions. Furthermore, the series $\text{M}(\text{N}_3)_3$, $\text{M}(\text{N}_3)_3 \cdot \text{CH}_3\text{CN}$, $[\text{M}(\text{N}_3)_4]^-$, $[\text{M}(\text{N}_3)_5]^{2-}$, and $[\text{M}(\text{N}_3)_6]^{3-}$ ($\text{M} = \text{Ga}, \text{In}, \text{Tl}$) was studied by theoretical calculations. The Group 13 azides are of special interest as precursors for semiconductor and opto-electronic materials, and our paper was highlighted on the cover of *Angewandte Chemie*.¹⁹

The Group 15 azides are of significant interest as a green replacement for the highly toxic lead diazide in primary explosives. The binary polyazides, $\text{As}(\text{N}_3)_3$, $\text{Sb}(\text{N}_3)_3$ and $\text{Bi}(\text{N}_3)_3$ were prepared and stabilized by either anion or donor-acceptor adduct formation. Crystal structures were obtained for $[\text{Bi}(\text{N}_3)_4]^-$, $[\text{Bi}(\text{N}_3)_5]^{2-}$, $[\text{bipyBi}(\text{N}_3)_5]^{2-}$, $[\text{Bi}(\text{N}_3)_6]^{3-}$, $\text{bipyAs}(\text{N}_3)_3$, $\text{bipySb}(\text{N}_3)_3$ and $[(\text{bipy})_2\text{Bi}(\text{N}_3)_3]_2$. An interesting feature of these pnictogen(+III) compounds is the presence of a free valence electron pair on the central atom which can be either sterically active or inactive. The $[\text{Bi}(\text{N}_3)_5]^{2-}$ anion possesses a sterically active, free Bi valence electron pair and a monomeric, pseudo-octahedral structure with a coordination number (CN) of six, whereas its bipyridyl adduct has a pseudo-monocapped trigonal prismatic structure with CN 7 and a sterically inactive free valence electron pair. Due to the high oxidizing power of $\text{Bi}(+\text{V})$, reactions aimed at synthesizing the binary $\text{Bi}(+\text{V})$ azides, $\text{Bi}(\text{N}_3)_5$, and $[\text{Bi}(\text{N}_3)_6]^-$, resulted in the reduction to $\text{Bi}(+\text{III})$ compounds by $[\text{N}_3]^-$. Because of the difficulty in growing single crystals of polymeric, free $\text{Bi}(\text{N}_3)_3$, its X-ray diffraction powder pattern was recorded at room temperature. This pattern is very distinct from that calculated for $\text{Sb}(\text{N}_3)_3$ from its single crystal data recorded at 223 K. The crystal structure of the bis-bipyridyl adduct, $[(\text{bipy})_2\text{Bi}(\text{N}_3)_3]_2$, was successfully

determined. It is dimeric and derived from two square BiN_8 antiprisms sharing an edge consisting of two $\mu^{1,1}$ -bridging N_3 ligands and with Bi having CN 8 and a sterically inactive, free valence electron pair. The novel $\text{bipyAs}(\text{N}_3)_3$ and $\text{bipySb}(\text{N}_3)_3$ adducts were also prepared and structurally characterized. They are monomeric and isostructural, and they contain a sterically active, free valence electron pair on their central atom with CN 6. A systematic analysis of the structures of these polyazides was carried out and is supported by electronic structure calculations. The results of the electronic structure calculations suggest that the M06-2X density functional is well suited for the prediction of steric activity of free valence electron pairs in main-group chemistry. Furthermore, it was found that the solid-state structures can strongly differ from those of the free gas-phase species or of those in solutions, and that free valence electron pairs which are sterically inactive in a chemical surrounding can become activated in the free isolated species.²⁰

The arrangement of the azido ligands in the pseudo-trigonal bipyramidal $[\text{As}(\text{N}_3)_4]^-$ and $[\text{Sb}(\text{N}_3)_4]^-$ anions theoretically can give rise to 7 different conformers which have identical MN_4 skeletons but different azido ligand arrangements and very similar energies. We have synthesized and structurally characterized five of these conformers by subtle variations in the nature of the counter ion. Whereas conformational variability is common in organic chemistry, it is rare in inorganic main group chemistry and is usually limited to two. To our best knowledge, the experimental observation of five distinct single conformers for the same type of anion is unprecedented. Theoretical calculations at the M06-2X/cc-pwCVTZ-PP level for all seven possible basic conformers show that (1) the energy differences between the five experimentally observed conformers are about 1 kcal/mol or less, and (2) the free monomeric anions are the energetically favored species in the gas phase and also for $[\text{As}(\text{N}_3)_4]^-$ in the solid state, whereas for $[\text{Sb}(\text{N}_3)_4]^-$ associated anions are energetically favored in the solid state and in solutions. Raman spectroscopy shows that in the azide antisymmetric stretching region, the solid-state spectra are very distinct for the different conformers and permit their identification. The spectra of solutions are solvent dependent and differ from those of the solids indicating the presence of rapidly exchanging equilibria of different conformers. The only compound for which a solid with a single well-ordered conformer could not be isolated was $[\text{N}(\text{CH}_3)_4][\text{As}(\text{N}_3)_4]$ which formed a

room-temperature, viscous, ionic liquid. Its Raman spectrum was identical to that of its CH₃CN solution indicating the presence of an equilibrium of multiple conformers.²¹

Another interesting feature of group 15 azides was the fact that, based on a recent crystallographic study²², P(C₆H₅)₄N₃ and As(C₆H₅)₄N₃ in the solid state have ionic [M(C₆H₅)₄]⁺N₃⁻ type structures, whereas Sb(C₆H₅)₄N₃ exists as a pentacoordinated covalent solid. Using the results from density functional theory, lattice energy (VBT) calculations, sublimation energy estimates, and Born-Fajans-Haber cycles, it is shown that the maximum coordination numbers of the central atom M, the lattice energies of the ionic solids, and the sublimation energies of the covalent solids have little or no influence on the nature of the solids. Unexpectedly, the main factor determining whether the covalent or the ionic structures are energetically favored, is the first ionization potential of [M(C₆H₅)₄]. The calculations show that at ambient temperature the ionic structure is favored for P(C₆H₅)₄N₃ and covalent structures are favored for Sb(C₆H₅)₄N₃ and Bi(C₆H₅)₄N₃, while As(C₆H₅)₄N₃ presents a borderline case.²³

Theoretical Calculations

High-level theoretical studies of nitrogen, oxygen, selenium and halogen fluorides, oxides and oxofluorides were carried out which provide reliable thermodynamic values for these important compounds. These studies provide valuable insight as to which of the still missing compounds are thermodynamically and kinetically feasible and should be pursued synthetically.²⁴⁻²⁷

Furthermore, the nature of lone pair domains is a fascinating problem which previously has received only very little attention. The lone pair lies at the very heart of chemistry, and is often in a conceptual respect the site of chemical reactivity. We have addressed the problem of characterizing lone pair electrons using quantum chemical topology methods. After demonstrating that the commonly used Quantum Theory of Atoms in Molecules (QTAIM) does not provide a convincing physical basis for Lewis theory in cases involving heavy main group atoms, we have introduced a novel approach for chemically meaningful quantification of lone pair domains. We have shown that that the topological analysis of the Electron Localization Function (ELF) 10 can be improved upon by the introduction of intra-basin partitioning, and we

have defined a quantity named High ELF Lone pair basin Population (HELP), which probes the more chemically relevant and electronlocalized volumes of the lone pair domain. This approach has revealed strong correlations between HELP and a range of physical properties and quantum mechanical constructs, such as the electrostatic surface potential, electron affinity, proton affinity, ionization potential, HOMO and LUMO energies, atomic charge, as well as *s*-character of Natural Bond Orbital (NBO) lone pair orbitals, and molecular geometry. A strong connection between topological density and orbital-based analysis of chemistry is intuitively expected, but has until now not been demonstrated. This is the first time that an average electron population, obtained by any localization method, has been shown to correlate with physical and chemical properties of molecules. The application of HELP as a descriptor of lone pairs is predicted to be of general use. The results and conclusions of this study have been thoroughly validated by analyzing characteristics of 55 main group molecules, encompassing all elements of periods 2-6 in groups 15 to 17.²⁸

Azole Chemistry

In connection with an ongoing ONR program, we have carried out interesting tetrazole chemistry which has resulted in novel high-oxygen carriers for green ammonium perchlorate replacements.^{29,30}

Miscellaneous

An invited viewpoint article on Neil Bartlett's historic discovery of noble gas compounds was written for Chem. Commun.,³¹ and two book chapters on the first chemical synthesis of elemental fluorine and the Preparation of Transition Metal Fluorides using ClF₃ were written.³²

Archival Publications

- (1) Christe, K. O.; Haiges, R.; Wilson, W. W.; Boatz, J. A., "Synthesis and Properties of N₇O⁺", Inorganic Chemistry, p. 1245, vol. 49, (2010).
- (2) Craciun, R.; Long, R. T.; Dixon, D. A.; Christe, K. O., "Electron Affinities, Fluoride Affinities, and Heats of Formation of the Second Row Transition Metal Hexafluorides: MF₆ (M = Mo, Tc, Ru, Rh, Pd, Ag)", J. Chem. Phys. A, p. 7571, vol. 114, (2010).

- (3) Christe, K. O.; Dixon, D. A.; Grant, D. J.; Haiges, R.; Tham, F. S.; Vij, A.; Vij, V.; Wang, T.-H.; Wilson, W. W., "Dinitrogen Difluoride Chemistry. Improved Syntheses of *cis*- and *trans*-N₂F₂, Synthesis and Characterization of N₂F⁺Sn₂F₉⁻ Ordered Crystal Structure of N₂F⁺Sb₂F₁₁⁻, High-Level Electronic Structure Calculations of *cis*-N₂F₂, *trans*-N₂F₂, F₂N=N, and N₂F⁺, and Mechanism of the *trans-cis* Isomerization of N₂F₂", *Inorganic Chemistry*, p. 6823, vol. 49, (2010).
- (4) Haiges, R.; Boatz, J. A.; Christe, K. O., "The Synthesis and Structure of the Vanadium(IV) and Vanadium(V) Binary Azides V(N₃)₄, [V(N₃)₆]²⁻, and [V(N₃)₆]⁻", *Angew. Chem. Int. Ed.*, p. 8008, vol. 49, (2010).
- (5) Grant, D. J.; Wang, T.-H.; Vasiliu, M.; Dixon, D. A.; Christe, K. O., "F⁺ and F⁻ Affinities of Simple N_xF_y and O_xF_y Compounds", *Inorganic Chemistry*, p. 1914, vol. 50, (2011).
- (6) Haiges, R.; Boatz, J. A.; Williams, J. M.; Christe, K. O., "Preparation and Characterization of the Binary Group 13 Azides M(N₃)₃ and M(N₃)₃ • CH₃CN (M = Ga, In, Tl), [Ga(N₃)₅]²⁻, and [M(N₃)₆]³⁻ (M = In, Tl)", *Angewandte Chemie-International Edition*, p. 8828, vol. 50, (2011).
- (7) Christe, K. O.; Haiges, R.; Boatz, J. A.; Jenkins, H. D. B.; Garner, E. B.; Dixon, D. A., "Why are [P(C₆H₅)₄]⁺N₃⁻ and [As(C₆H₅)₄]⁺N₃⁻ Ionic Salts and Sb(C₆H₅)₄N₃ and Bi(C₆H₅)₄N₃ Covalent Solids? A Theoretical Study Provides an Unexpected Answer," *Inorganic Chemistry*, p. 3752, vol. 50, (2011).
- (8) Haiges, R.; Rahm, M.; Dixon, D. A.; Garner, III, E. B.; Christe, K. O., "Binary Group 15 Polyazides. Structural Characterization of [Bi(N₃)₄]⁻, [Bi(N₃)₅]²⁻, [bipyBi(N₃)₅]²⁻, [Bi(N₃)₆]³⁻, bipyAs(N₃)₃, bipySb(N₃)₃, and [(bipy)2Bi(N₃)₃]₂ and on the Lone Pair Activation of Valence Electrons," *Inorganic Chemistry*, p. 1127, vol. 51, (2012).
- (9) Jackson, V. E.; Dixon, D. A.; Christe, K. O., "Thermochemical Properties of Selenium Fluorides, Oxides, and Oxofluorides," *Inorganic Chemistry*, p. 2472, vol. 51, (2012).
- (10) Thanthiriwatte, K. S.; Vasiliu, M.; Dixon, D. A.; Christe, K. O., "Structural and Energetic Properties of Closed Shell XF_n (X = Cl, Br, and I; n = 1-7) and XO_nF_m (X = Cl, Br, and I; n = 1-3; m = 0-6) Molecules and Ions Leading to Stability Predictions for Yet Unknown Compounds," *Inorganic Chemistry*, p. 10966, vol. 51, (2012).

- (11) Haiges, R.; Rahm, M.; Christe, K. O., "Unprecedented Conformational Variability in Main Group Inorganic Chemistry: the Tetraazidoarsenite and -Antimonate Salts $A^+[M(N_3)_4]^-$ ($A = NMe_4, PPh_4, (Ph_3P)_2N$; $M = As, Sb$), Five Similar Salts, Five Different Anion Structures," *Inorganic Chemistry*, p. 402, vol. 52, (2013).
- (12) Christe, K. O., "Bartlett's discovery of noble gas fluorides, a milestone in chemical history," *Chem. Commun.*, p. 4588 (2013).
- (13) Haiges, R.; Bigler Jones, C.; Christe, K. O., "Energetic Bis(3,5-dinitro-1*H*-1,2,4-triazolyl)dihydro- and dichloroborates and Bis(5-nitro-2*H*-tetrazolyl)-, Bis(5-trinitomethyl-2*H*-tetrazolyl)-, and Bis(5-fluorodinitromethyl-2*H*-tetrazolyl)dihydro-borate," *Inorganic Chemistry*, p. 402, vol. 52, (2013).
- (14) Haiges, R.; Christe, K. O., "Energetic High-Nitrogen Compounds: 5- (Trinitromethyl)- 2*H*- tetrazole and -tetrazolates, Preparation, Characterization, and Conversion into 5- (Dinitromethyl)tetrazoles," *Inorganic Chemistry*, p. 7249, vol. 52, (2013).
- (15) Rahm, M.; Christe, K. O., "Quantifying the Nature of Lone Pair Domains," *Chem. Phys. Chem.*, early view, DOI: 10.1002/cphc.201300723 (2013).

Books or Other One-time Publications

Christe, K. O., "Preparation of Elemental Fluorine," Contributed Chapter to Book on "Efficient Preparations of Fluorine Compounds," p. 1, John Wiley & Sons, Inc., Hoboken, New Jersey 2013, ISBN 978-1-118-07856-3.

Haiges, R., "Preparation of Transition Metal Fluorides using ClF_3 ," Contributed Chapter to Book on "Efficient Preparations of Fluorine Compounds," p. 100, John Wiley & Sons, Inc., Hoboken, New Jersey 2013, ISBN 978-1-118-07856-3.

Conference Papers

Twenty nine invited lectures were presented in the course of this three year program at national and international Conferences.

Honors

Arthur Adamson Award, (2013), M. Rahm;

B. Douda Award, International Pyrotechnic Society, (2013), M. Rahm;

R. Bau Award, (2012), R. Haiges;

ACS Tolman Award (2011), K. Christe;

Election to the European Academy of Sciences and Arts, Salzburg, Austria, (2011), K. Christe;

Election to the European Academy of Sciences, Liege, Belgium, (2010), K. Christe.

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